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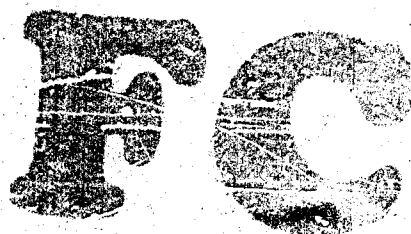
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TECHNICAL REPORT

to the

OFFICE OF NAVAL RESEARCH

on

THE INVESTIGATION OF THE NATURE OF THE FORCES OF ADHESION

Contract No. N0001-60-00000
Project No. 001-356

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ABSTRACT

A study of the interphase between organic coatings and the metallic substrate has been continued. The use of infrared analysis of lacquer solutions is described as adaptable to multicomponent systems.

Adsorption isotherms were determined for aluminum oxide in vinyl acetate-chloride copolymer solutions. Experimental procedures were developed by which the amount of lacquer component adsorbed from solution by aluminum oxide could be determined by comparison of the infrared analysis of the solution before and after shaking with the oxide. In the cases investigated, it was found that the greatest adsorption of vinyl chloride-acetate copolymers occurred with the film former recognized as providing the greatest adhesion. The infrared procedure can be extended to multicomponent systems where the analytical methods used earlier were limited by requiring as many separate analysis as there were components.

Preliminary investigation of the strength of the bonds formed in the interphase has been started. Study of the nature of the interphase was initiated through the construction of a dual calorimeter system for the measurement of relative heats of immersion of aluminum oxide in solutions of lacquer ingredients. Heat of immersion measurements of aluminum oxide in solutions of lacquer ingredients promises to provide valuable and much needed quantitative information about the nature of the interphase.

FOREWORD

This is the sixth annual report of the investigation of the physical-chemical nature of adhesion of organic coatings to non-ferrous metals by Professor L. Reed Brantley and co-workers.

Two articles have been published and five papers have been presented before the division of Paint, Plastics and Printing Ink Chemistry of the American Chemical Society. The papers have been printed in full in the Preprint Booklets prepared each fall and spring for the members of the Division. Some of the booklets are still available and can be obtained from the Secretary of the Division. Photostatic copies of the papers can be obtained from libraries which maintain complete files of the Division Preprint Booklets, Such as the New York City Public Library. The titles are listed below.

1. "Nature of the Adhesion of Lacquers to Non-Ferrous Metals." XII International Congress of Pure and Applied Chemistry, Sept. 10 - 13, 1951.
2. "Adhesion of Lacquers to Non-Ferrous Metals," L. Reed Brantley, Arthur Woodward and Gordon Carpenter, Ind. and Eng. Chem., 44 2289, 1952.
3. "Modern Theories of Adhesion," L. Reed Brantley and Gordon Carpenter, Official Digest, Fed. Paint and Varnish Production Clubs, 374 57, 1952.
4. "Method of Removal of Coatings by the Adherometer and Improvement in its Design," Preprint Booklet, Vol. 13, No.1, pp. 140-2, March 1953.
5. "A Statistical Study of the Operation and Design of the Adherometer and the Resulting Changes," Preprint Booklet, Vol. 14, No.1, pp. 1 - 5, March 1954.
6. "A Study of the Adhesion to Aluminum of an Ethylcellulose Lacquer in Relation to Certain of its Film Properties," Preprint Booklet, Vol. 14, No. 2, pp. 45 - 8, September 1954.
7. "The Adsorption of Lacquer Components on Aluminum Oxide," Preprint Booklet, Vol. 15, No. 1, pp. 20 - 6, April 1955.

8. "The Relation Between Adherometer Adhesion, Bulk Shear and Other Film Properties of Ethylcellulose Coatings," Preprint Booklet, Vol. 15, No. 2, pp. 34 - 40, September 1955.
9. "The Investigation of the Nature of the Forces of Adhesion," Annual Report for O. N. R. Contract for 1954 - 55, available through the U. S. Department of Commerce, Washington 25, D. C. in printed form as O. T. S. Identification Number: P. R. 121555. \$2.25.

The Study of the adhesion of organic coatings to metallic substrates has been resolved into the investigation of three types of failure, namely: cohesive failure in the metallic substrate; cohesive failure in the organic coating; and adhesive failure in the interface which we prefer to call the interphase separating the two. The earlier work concentrated on the investigation of the nature of the failure in the coating by means of adherometer adhesion or "hesion" measurements made with modifications of the Interchemical Adherometer. A study of the cohesive failure in the substrate is considered to be outside of the present field of investigation. This places the study of the nature of the interphase next in importance in this program of the investigation of the principles of adhesion.

A preliminary investigation of the nature of the interphase was undertaken with the assistance of Barbara Scott. This took the form of experiments to determine the relative amounts of lacquer ingredients which are adsorbed on aluminum oxide, which makes up the substrate of an aluminum surface. This report describes the continuation of the adsorption studies of film formers.

INTRODUCTION

It is proposed that the initial adsorption at the liquid/solid interface and the resulting change in internal energy measured as the energy of adhesion determines the final value of the air-dry adhesion. The above statement should be modified to correct for the effect of film properties which developed upon evaporation of solvent. However, measurements made of the relative amounts of film former at the interface of the liquid/solid system will give valuable information with which to predict air-dry adhesion. Air-dry adhesion may be defined as the attractive force between a protective film formed by the evaporation of the solvent from a lacquer and the surface to which the lacquer was applied.

The research work was divided into two projects which proceeded simultaneously. One project was undertaken to compare heat of immersion isotherms of VMCH and VYHH which are film formers of vinyl chloride-acetate copolymers. VMCH has excellent air-dry adhesion and VYHH has poor air-dry adhesion on clean, smooth metal. A differential calorimeter was built using thermistors as the temperature sensitive elements. The calorimeter was calibrated to an overall accuracy of 5% for temperature increases up to 0.01°C . The temperature increases expected upon immersion of alumina in a copolymer solution is about 0.01°C . Thus, the sensitivity of the calorimeter is adequate

for heat of immersion measurements. However, difficulties in experimental procedures have delayed investigations of heat of immersion isotherms.

In the second part of the project, adsorption isotherms were obtained for VMCH and VYHH. A comparison of isotherms showed that high adsorption was indicative of excellent, air-dry adhesion and conversely that low adsorption was related to poor, air-dry adhesion.

I

LITERATURE SURVEY

Definition of Terms

Adhesion is defined in Hatch's Chemical Dictionary as the attraction or force which holds unlike molecules together. This general definition will be used throughout this thesis.

Adsorption is the ability of a substance (adsorbent) to hold or concentrate gases, liquids or dissolved substances (adsorbate) upon its surface, a property due to adhesion, *q.v.*: hence, producing a change of concentration of the adsorbate on the surface of the adsorbent with respect to the interior concentration of the adsorbate.¹

The heat of immersion is the heat evolved when a clean, finely divided, outgassed solid is immersed in a liquid. The reverse process is the heat of emersion.

The work of adhesion (W_A) and the energy of adhesion (h_A) are by definition the increase in free and internal energy, respectively, involved in the separation of unit area of the liquid from the solid when no trace of adsorbed film is left on the surface of the solid. The actual process is always carried out in the reverse direction beginning with clean solid in a vacuum.²

General Theories of Adhesion

There are three theories of adhesion. These theories include what most research chemists agree are the important factors in bonding. As yet there is no agreement on a general theory of adhesion that would explain why all adhesives adhere to surfaces.

The first theory suggests that adhesion is due to molecular attraction. All matter contains electrical forces in excess of those needed to hold the atoms within a molecule together. These tiny electrical forces are capable of providing a very strong attraction between the adhesive film and the surfaces to be bonded.

Chemical reaction is also believed responsible for bonding. In some instances, the adhesive reacts chemically with the surfaces of the material to be bonded. A chemical bond is formed which holds the two materials together.

With porous materials, the adhesive fills the pores of the materials being bonded. When the adhesive hardens, it interlocks the two materials together.

Energy of Adhesion and Heat of Immersion

The method for the direct determination of the important term used in the calculation of the total energy of adhesion involves immersion of the finely divided solid in the liquid contained in an extremely sensitive calorimeter. Since the energy of immersion of the clean surface is desired, the solid should be outgassed at as high a temperature as can be employed without affecting the surface.

Calorimetric determinations can be made of heat of immersion of a metallic powder in liquid. By performing auxiliary experiments, the data obtained can be used to give the energy required to separate a solid from a liquid (energy of adhesion). These experiments are the accurate measurement of the surface area of the powder and the determination of the variation of surface energy of a liquid with temperature.³

The change in internal energy involved where a liquid is separated from a solid at their interface to give clean surfaces of both the solid and liquid, is the energy of adhesion. The energy of adhesion $\epsilon_{A(sL)}$ is:

$$\epsilon_{A(sL)} = \epsilon_s - \epsilon_{sL} + \epsilon_L = \epsilon_E + \epsilon_L$$

that is, the energy of adhesion is simply equal to the heat of immersion plus the surface energy of the liquid. The surface energy of the liquid is given by the Gibbs-Helmholtz equation:

$$\epsilon_L = \gamma - T \frac{d\gamma}{dT}$$

Where

γ = the surface tension of the liquid

T = the absolute temperature

$\frac{d\gamma}{dT}$ the variation of surface tension of the liquid with temperature

The Nature of Adsorption

Adsorption is the process by which the atoms or molecules of one material become attached to the surface of another or, in a more general sense, become concentrated at an interface. This definition does not make any statement about the mechanism involved in either physical or chemical adsorption.

While in applying the hypothesis concerning the molecular fields, the intensity of the stray field around the molecules is of primary importance, at least one additional principle must be used if the direction which any change will take by itself is to be predicted. As might be expected, the second law of thermodynamics is of fundamental importance in this connection, and for this purpose it may be stated in the form: any change which takes place by itself in a system will proceed in the direction which will result in a decrease in the free energy of the system. Thus a surface will tend to decrease in area. Since a rapid variation of the intensity of the stray field with the distance in any direction is accompanied by a high concentration of free energy, the second law indicates that in any change which takes place by itself, the variation in the stray field become less abrupt.⁵

The following discussion of the orientation of molecules in a liquid/liquid system may be analogous to the liquid/solid system except that the solid usually displays a highly oriented crystalline surface.

"The molecules in the surfaces of liquids seem to be oriented,

and in such a way that the least active or least polar groups are oriented toward the vapor phase: IF WE SUPPOSE THE STRUCTURE OF THE SURFACE OF A LIQUID TO BE AT FIRST THE SAME AS THAT OF THE INTERIOR OF THE LIQUID, THEN THE ACTUAL SURFACE IS ALWAYS FORMED BY THE ORIENTATION OF THE LEAST ACTIVE PORTION OF THE MOLECULE TOWARD THE VAPOR PHASE, AND AT ANY SURFACE OR INTERFACE THE CHANGE WHICH OCCURS IS SUCH AS TO MAKE THE TRANSITION TO THE ADJACENT PHASE LESS ABRUPT. This last statement expresses a general law, of which the adsorption law is a special case".⁶

Physical and Chemical Adsorption

Physical adsorption or van der Waal's adsorption, states that molecules are held to the surface by physical forces which correspond to those involved in the van der Waal's equation of state for gases. In chemisorption, the adsorbed molecules are held to the surface by valence forces of the same nature as those which bind atoms together in molecules.

There are characteristics which distinguish physical from chemical adsorption. The heat evolved when physical adsorption occurs is usually similar to the heat of liquefaction of a gas, i. e., a few hundred cal per mole, and the reactivity of the adsorbed substance is consequently not markedly altered. The forces involved in chemisorption are much stronger than those in van der Waal's adsorption, and the heats evolved

are of the same order as those liberated in chemical reactions, values of 10 to 100 kcal per mole being common. Physical adsorption is easily reversible in contrast to chemisorption which is irreversible or reversible only with great difficulty. Furthermore, physical adsorption is essentially non-specific with respect to the adsorbent and adsorbate, whereas chemisorption involves a high degree of specificity.⁷

Another criteria for physical adsorption is that physical adsorption decreases with rising temperature. The kinetic theory explains why this may be so; the kinetic movement of adsorbed atoms or molecules increase with increasing temperature, and the substance adsorbed, therefore, tends to leave the adsorbent. Low temperatures favor still more adsorption, because the thermal oscillations of adsorbed molecules are weakened enabling the van der Waal's forces to be more effective.

Contrary to the case of physical adsorption, chemisorption increases with increasing temperature.⁸ This increase is expected in chemical reactions, of which chemisorption is a special case limited to surface reaction, for the rate of reaction doubles or triples for every ten degree rise in temperature.

Adsorption Isotherms

In recent years, much has been concentrated on effort to describe adsorption in terms of isotherms and to analyse different types of such isotherms. An adsorption isotherm is the relationship between the

amount adsorbed per gram of adsorbent at equilibrium and the pressure for a gas/solid system. An adsorption isotherm for a solution/solid system is the relationship between the amount of solute adsorbed per gram of adsorbent and the equilibrium concentration of the solution at constant temperature.

Adsorption isotherms have in many cases been fitted to equations, and Table I summarizes some of the more important equations that have been employed. Some of these equations have a theoretical basis, while others are purely empirical, as has been indicated in the last column. It was noted that the Freundlich's isotherm equation is not only the simplest but a more general equation for it is applicable to physical and chemical adsorption. Furthermore, this relationship has theoretical as well as empirical confirmation, 9, 10, 11, 12

If in a liquid/solid system one assumes that the solute obeys the ideal gas laws or van't Hoff's law in dilute solution, the applicability of Freundlich's equation may be substantiated by its conversion into logarithmic form:

$$a \approx k c^{1/n}$$

$$\log a \approx 1/n \log c + \log k$$

where a = amount adsorbed

c = equilibrium concentration

k = a constant

n = a constant greater than 1

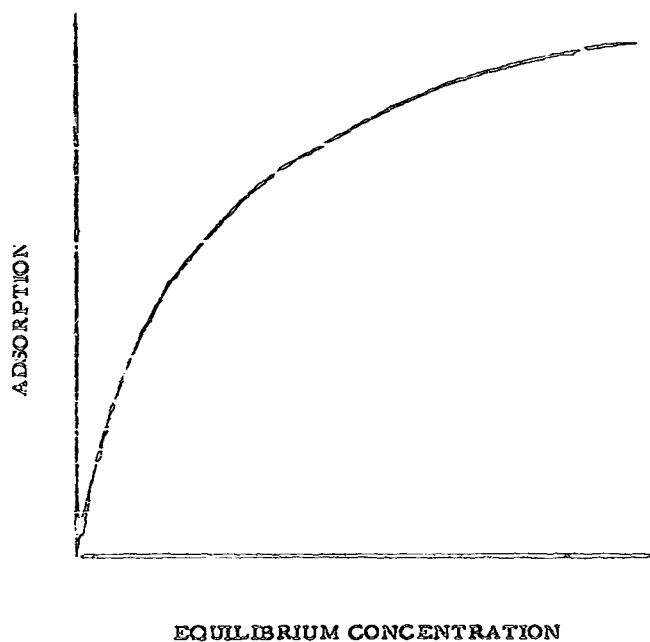


FIGURE 1

Normal Adsorption Isotherm in Liquid/Solid System
According to Wo. Ostwald and de Izaguirre.¹³

Table 1. Adsorption Isotherm Equations 12

v = volume adsorbed; p = gas pressure; θ = fraction of surface covered; v_m = volume of gas required to form a unimolecular layer. The remaining symbols represent constants.

Name	Isotherm	Remarks	Ref.
Freundlich	$v = kp^{1/n}$ (n greater than 1)	Empirical, but has been interpreted theoretically, as van der Waals adsorption and chemisorption	1
Chakravart-Dhar	$v = \frac{kp^{1/n}}{b + p^{1/n}}$	Empirical; unimolecular layer; chemisorption	2
Langmuir	$\theta = \frac{bp}{1 + bp}$	Theoretical; unimolecular layer; chemisorption	3
William-Henry	$\ln \frac{v}{p} = a + b \ln v - \frac{bv}{v_m}$	Theoretical; unimolecular layer; chemisorption	4
Zeise	$v = \frac{av}{1 + kp} \quad 1/2$	Theoretical; unimolecular layer; chemisorption	5
Magnus	$v = \frac{k_1 k_2 p^2 - k_3 v^2}{1 + k_1 p - \frac{k_3 v^2}{k_2}}$	Theoretical; unimolecular layer; van der Waals adsorption	6

Table 1 - Continued

Name	Isoborn	Remarks	Ref.
die Boor-Zucker	$\ln p = K_2 K_1 \sqrt{m}$ $\frac{1}{p}$	Theoretical; polymericular layer; von der Waals adsorption	7
Diamin-Silphen	$\ln \frac{p}{p_0} = \frac{1}{2} \ln \frac{c_0 p}{p_0}$	Theoretical; unimolecular adsorption	8
Brommer-Harnett-Toller	$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} \ln \frac{p}{p_0}$	Theoretical; polymericular layer; von der Waals adsorption	9

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- * Limon quantities derived: Mergon B., and Strumano, Kolloid Chemistry
M., E., John Wiley and Sons, Inc., New York, pp 76, 77, 85
- oo Zeldovich, J., Acta Physicochim., U.S.S.R., 1, 961 (1935); Dawson, J., and Zundth, A. N. L.,
J. Chem. Phys., 51, 260-2 (1954)

If the plot of $\log a$ versus $1/n \log c$ ($\log k$ is a constant) yields a straight line the concurrence with Freundlich's equation over a limited range of concentration is accomplished. The values of the constants k and $1/n$ can be obtained for each case by graphical extrapolation.

Further study of the adsorption phenomena showed, however, that the lines obtained by the logarithmic plot were not always straight lines, especially at higher concentrations of adsorbate.

Adsorption isotherms retain their shapes with increasing temperature although a decrease in the adsorption maximum indicates the decrease in physical adsorption.¹³

II

INVESTIGATION
OF THE
HEAT OF IMMERSION OF METALLIC POWDER
IN SOLUTION OF FILM FORMER

The relation between heat of immersion and concentration of VYHH vinyl chloride-acetate copolymer, is best shown by a heat of immersion isotherm. This isotherm is a graph of the heat of immersion and the concentration of film former. Another isotherm is needed for a similar concentration range for VMCH vinyl chloride-acetate copolymer in order to compare these two polymers. These film formers were selected because they have different air-dry adhesion. Thus, a comparison of these isotherms should suggest a positive or negative correlation between heat of immersion and air-dry adhesion.

Procedure

A differential calorimeter was built^{15,16,17} using thermistors as the heat sensitive elements (Figure 16). The thermistors served as two resistance arms in a Wheatstone bridge and a high sensitivity potentiometer was used to detect the increase in temperature upon immersion of finely divided aluminum oxide in the lacquer. The procedure required that a thin walled, glass bulb containing the aluminum oxide sample be broken in a lacquer. Stirring was vigorously maintained to

effect a rapid dispersion of the powder and thereby more rapid evolution of heat.

The values of heat of immersion were highly sensitive to temperature and to impurities in the powder and lacquer. Temperature variations were minimized by using a calorimeter constructed with two identical cells; one cell was used as a reference and the other as the test cell. Thus, any room temperature fluctuation affected both cells equally and, consequently, a null in the bridge could be maintained more easily. The effect of impurities were minimized by obtaining enough powder, solvent, and resin so that the same source of materials could be utilized throughout the investigation.

The aluminum oxide was of reagent grade. Technical grade ethylene dichloride and commercially available resins were used.

There were two preliminary experiments which had to be performed before an isotherm could be plotted. First, the instrument was calibrated. Second, an experiment had to be performed to determine the heat evolved upon breaking an empty glass bulb. Only upon satisfactory evaluation on completion of these two experiments could the determinations of heat of immersion confidently proceed.

A quantity of 1000 ml of distilled water in the calorimeter was brought to approximate thermal equilibrium by means of the heaters and slight adjustments of stirring rates as proved necessary. Sufficient time was allowed until the slope of the time-temperature curve was not more than 20 microvolt per minute. The experiment represented in Figure 5 was an exception. This took about an hour. Thermistor readings were made for six to eight consecutive minutes and then current was applied to the heater in the test cell. The exact time at which the current was applied and turned off was noted. After this heating period, thermistor readings were continued for six more minutes without interruption. This identical heating technique was repeated two or three more times. On other graphs, the entire procedure was repeated, however, with the application of a greater amount of electrical energy. The three temperature increases correspond to the three points on the calibration curve. Extrapolations to obtain the temperature change were made to the center of the heating periods. The difference in the temperature was measured with dividers as the difference in microvolts between the extrapolated lines.

A large graph is advantageous in recording the temperature increase caused by breaking the glass bulb and the immersion of alumina. This temperature increase is followed by several successive increases in order to calibrate the calorimeter and its contents. This procedure was repeated for each experiment.¹⁸

Interpretation of Results

Zettlemoyer, Young, Chessick and Healey reported that heats of immersion produced a temperature increase of 0.01°C .²⁰ This is equal to an evolution of about ten calories according to the calibration experiment. The earlier work of Boyd and Haskins substantiates the above mentioned investigation.²¹ The evolution of ten calories of heat can be measured with a precision of $22/1000$ in this region of the calibration curve.

The excess slope and consequent large heat is believed due to faulty technique in the procedure.

In the second preliminary experiment, difficulty was encountered when the heat value of bulb breakage was sought. Unfortunately, the increase in temperature did not reach a steady state but gradually continued to increase. Measurement of the increase in temperature was impossible. This gradual increase was believed due to the bit of glass scraping against the walls of the calorimeter and the stirrer. The consequent friction explained the continual heat increase.

It is obvious, due to the inability to measure the heat evolved upon breaking a bulb, that further investigations would be meaningless until this difficulty is surmounted. (See suggested future work.) The time required to overcome experimental difficulties in the calorimeter could not be predicted. Therefore it appeared more advantageous to concentrate efforts in adsorption investigations, for this phase of the

research program showed greater promise of success.

III

INVESTIGATION OF THE ADSORPTION OF FILM FORMER BY METALLIC POWDER FROM SOLUTION OF FILM FORMER

The purpose of the adsorption investigation was to obtain data for various adsorption isotherms. An isotherm illustrates quantitatively the adsorption of film former as a function of the equilibrium concentration. A comparison of adsorption isotherms for the vinyl chloride-acetate copolymers of known air-dry adhesion should aid in the concurrence of these adsorption isotherms with Freundlich's adsorption equation would greatly reinforce the experimental work and would permit theoretical interpretations of the isotherms.

Procedure

The vinyl chloride-acetate copolymers VMCH and VYHH were selected because they represent a wide difference in air-dry adhesions. VMCH and VYHH have excellent and poor air-dry adhesion, respectively, on clean, smooth metal. Both resins are of medium polymer weight. VYHH has a composition of 87% vinyl chloride and 13% vinyl acetate. The VMCH however, is modified with 1% interpolymerized dibasic acid and consists of 87% vinyl chloride and 12% vinyl acetate.²²

Standard, stock solutions of 10% VMCH were prepared by weighing the resin to the nearest milligram and by addition of ethylene dichloride. Concentrations from 0.5% to 10% were made volumetrically with a 10 ml.

calibrated syringe.

The alumina used was the anhydrous gamma form. To produce a mild reactivation, it was heated at 135° C. for at least 24 hours and allowed to cool to room temperature in a desiccator. A 10,000 g sample of the powder was then shaken with 20.0 ml of lacquer. A mechanical shaker was operated for eight to ten hours so that the alumina was thoroughly dispersed. The samples were centrifuged for half an hour or more to obtain a clear lacquer for analysis. Three samples were tested to determine adsorption at selected concentrations between 0.5% to 6%. A fourth sample was used as a control.

An analysis of the quantity of VMCH adsorbed by alumina was made with a Beckman IR-1 Spectrophotometer. This instrument was redesigned and modified for these analyses.

Two control samples were analysed; one control sample at the initial concentration of the test samples and another control sample of a lesser concentration. Then the three test samples were rapidly analysed. These test samples yield % transmission readings which lie between the % transmission readings of the control samples. A linear relation between % transmission and concentration of VMCH was assumed over the narrow range of concentration between the two control samples. The amount of adsorption was calculated as shown in the appendix.

A similar analysis was made with a lacquer of VYHH.

Reproducibility

The technique of analyzing a control or known samples along with unknowns was used to check the reliability of the instrument. If drift in the infrared spectrophotometer was detected, the analysis was repeated.

The experimental variations of each adsorption isotherm may be seen in Figure 1. The average deviation from the mean is indicated by a vertical line above and below any point. These points represent the average of three determinations. The average deviations of the equilibrium concentration are the same as those in the y-axis but are of little consequence for the unit measure of the x-axis represents fifty unit measures along the y-axis.

The large difference in the adsorption isotherms does not warrant a statistical analysis to test validity of the difference. In the future, however, a comparison of adsorption isotherms which have an overlap of average deviations may be necessary. Then the null hypothesis should be applied to determine whether a significant difference exists between the isotherms.

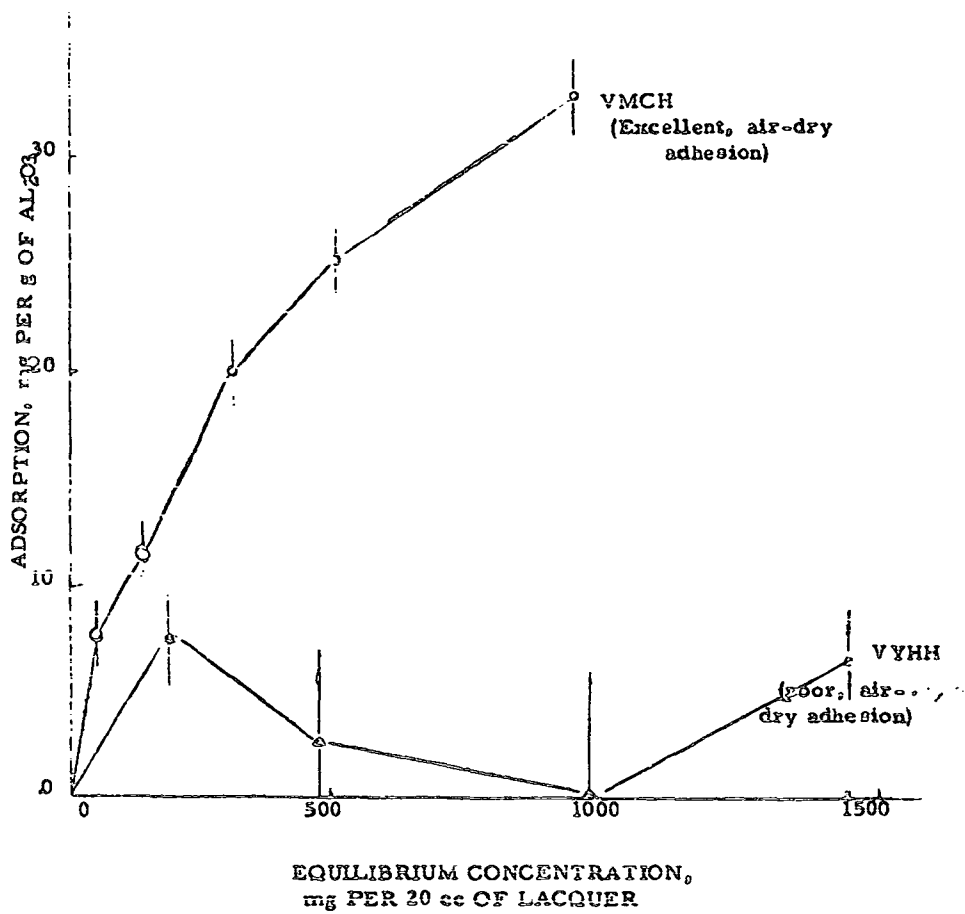


FIGURE 1

ADSORPTION ISOTHERMS OF VINYL CHLORIDE-ACETATE COPOLYMERS

TABLE II
 ADSORPTION ISOTHERMS FOR VINYL CHLORIDE-ACETATE
 COPOLYMERS IN ETHYLENE DICHLORIDE

Adsorption Isotherms from % Transmission Values (Calculated from Tables VI and VII)			
Initial Concentration, mg per 20 cc of lacquer	Average Adsorption mg per g Al_2O_3	Average Deviation, parts/1000	Equilibrium Concentrations (initial amount- adsorbed amount), mg per 20 cc of lacquer
125	7.5 \pm 1.4	190/1000	50
250	11.3 \pm 1.5	130/1000	137
VMCH 500	19.6 \pm 1.5	76/1000	304
750	24.6 \pm 1.5	61/1000	304
1250	32.3 \pm 2.1	64/1000	927
250	7.7 \pm 2.4	320/1000	173
500	2.5 \pm 4.4	—	475
VYHH 1000	0.0 \pm 3.9	—	1000
1500	6.3 \pm 2.00	320/1000	1437

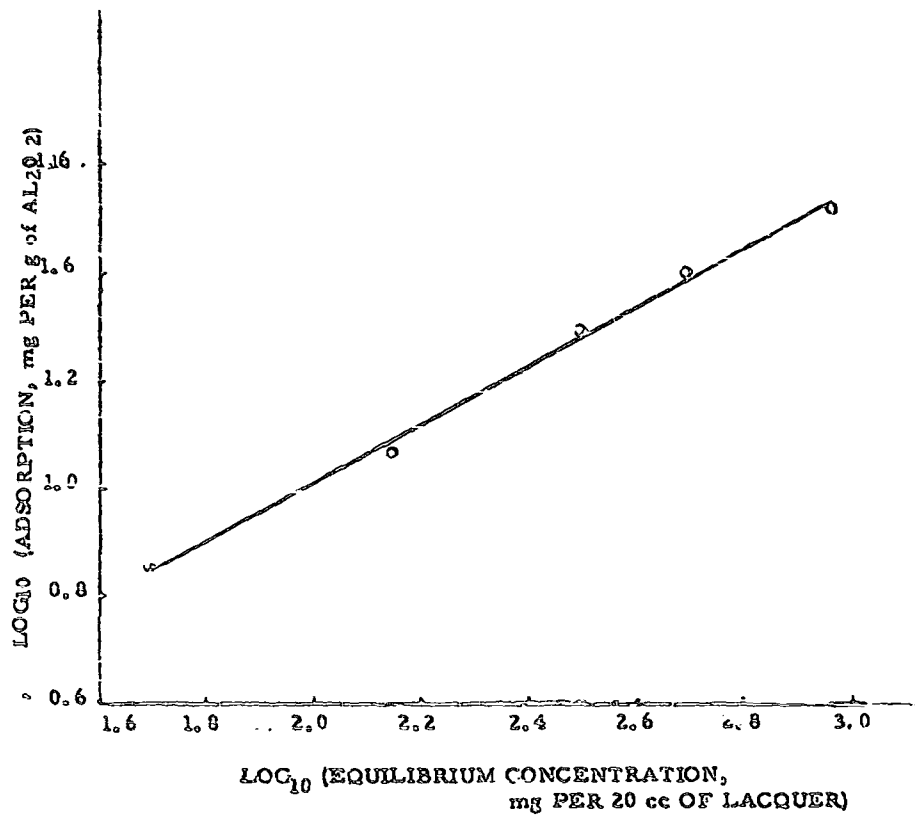


FIGURE 2

LOGARITHMIC PLOT OF THE ADSORPTION ISOTHERM FOR VMCH

TABLE III
LOGARITHMIC PLOT OF THE ADSORPTION ISOTHERM
OF VMCH

Initial Concentration, mg per 20 cc of lacquer	$\log_{10} a$ adsorption, mg per g Al_2O_3	$\log_{10} c_{eq}$ c_{eq} equilibrium concentration mg per 20 cc of lacquer
125	0.875	1.700
250	1.057	2.136
500	1.292	2.483
750	1.391	2.702
1250	1.509	2.967

Comparison of the Adsorption Isotherms of VMCH and VYHH

The comparison of adsorption isotherms is shown in Figure 1. Also, since the air-dry adhesion is known for VMCH and VYHH, the relation between high adsorption and air-dry adhesion is presented. Interpretation of Results

It can be seen in Figure 1 that a definite relation exists between air-dry adhesion and adsorption. The difference is significant for the average deviation from the mean (the vertical lines) are far from overlapping. High adsorption of about 25 mg/g of Al_2O_3 parallels excellent air-dry adhesion and adsorption of about a 2.5 mg/g of Al_2O_3 parallels poor air-dry adhesion.

The concurrence of the adsorption isotherm of VMCH to Freundlich's adsorption equation is shown in Figure 2. The logarithm of the quantity of VMCH adsorbed is plotted against the logarithm of the equilibrium concentration. Since all five of the points lie close to the straight line in Figure 2, the relationship shown for VMCH in Figure 1 is interpreted to obey Freundlich's equation. The adsorption exponent is 0.52.

IV

SUMMARY AND CONCLUSION

Heat of Immersion Investigation

A differential calorimeter for use in heat of immersion experiments was constructed. The calorimeter was calibrated for temperature increases from $0.0001^{\circ}\text{C}.$ to $0.01^{\circ}\text{C}.$ An overall precision of 5% was obtained for the calibration curve.

Another preliminary experiment was performed to determine the heat evolved upon breaking the glass bulb which would contain the metallic powder. Unfortunately, satisfactory results were not obtained because of the erratic nature of the friction between the broken glass and the walls of the calorimeter upon continued stirring. It is felt that this experimental difficulty can be surmounted in future experiments. (See suggested future work.)

The magnitude of the heats of immersion obtained by Zettlemoyer, Young, Chessick, and Henley could be measured with the calorimeter constructed. The earlier work of Boyd and Harkins resulted in evolution of similar magnitudes of heat. The possibility of comparison of air-dry adhesion with heats of immersion of different lacquers invites further investigation with the calorimeter.

Adsorption Investigation

An examination of the adsorption isotherms of VMCH and VYHH, established that a measureable relationship exists between air-dry adhesion and the quantity of VMCH adsorbed by alumina. High adsorption of VMCH was related to its excellent, air-dry adhesion. Conversely, poor adsorption of VYHH was related to its poor, air-dry adhesion.

The adsorption isotherm for VMCH was well fitted to Freundlich's equation.

In conclusion, the adsorption investigations gave a better understanding of adhesion. The writer proposes that high adsorption of a film former by metallic powder may be a measure of the consequent air-dry adhesion of the dried film. Also, the tabulation of the adsorption exponent $1/n$ of Freundlich's adsorption equation is suggested as a method with which to compare adsorption isotherms.

V

SUGGESTED FUTURE WORK

Heat of Immersion Investigation

1. The degree of solubility of alumina in lacquer should be investigated.
2. Friction created by broken glass from the bulb should be minimized.

It is suggested that the stirrers be raised one and a half inches above the bottom of each cell in the calorimeter to allow the glass to settle more easily. A slower stirring speed, which will still maintain uniform dispersion of alumina, is also suggested.

Adsorption Investigation

1. Information about the air-dry adhesion of other vinyl resins and other lacquers should be obtained from the manufacturers.
2. Adsorption isotherms of the vinyl chloride-acetate copolymers VYLF, VAGH, VYDR, VYNS-3 and the vinyl acetates AYAC, AYAA, AYAT should be investigated and plotted. A comparison of adsorption isotherms could then be made.
3. Conformity with Freundlich's equation as seen as a straight line in a log vs. log plot of the adsorption isotherm, should be noted. The value of the constant k and the adsorption exponent $1/n$ should provide a better comparison of adsorption isotherms.

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APPENDIX

SAMPLE CALCULATION FOR THE ELECTRIC ENERGY OF HEAT

The electric energy equivalent of heat is given by the equation:

$$H = \frac{I^2 R t}{k}$$

where H = heat (calories)
 I = current (amperes)
 R = resistance (ohms)
 t = time (minutes)
 k = constant (4.184 joules/calories)

An example is shown below. A current of 0.087 amperes was passed through a heater of 5.329 ohms for 99.9 seconds. The equivalent heat is:

$$H = \frac{(0.087)^2 (5.329) (99.9)}{4.184}$$

H 0.96 ± .03 calories.

TABLE IV

CALORIMETER CALIBRATION

Increase in Temperature, in microvolts, Caused by
the Application of Electrical Energy Equivalent to
One Calorie

Time, minutes	EMF, microvolts	Time, minutes	EMF, microvolts
0	0	0	331
2	40	8	252
3	0	9	252
6	6	10	247
7:30	0	11	230
8:30	0	12	230
9*	000	31	230
9:30	40	14:30	000
11:	55	15	245
11:30	34	15:30	254
12:	24	17	237
12:30	4	17:30	237
13	4	18	229
		19	234
		19:30	234
		20	234
		21	231

* Applied current of 0.087 amperes for 99.9 seconds

** Applied current of 0.087 amperes for 100.7 seconds

TABLE IV continued

CALORIMETER CALIBRATION

Increase in Temperature, in microvolts, Caused by the Application of Electrical Energy Equivalent to One Calorie	
Time, minutes	EMF, microvolts
0	233
1	204
2	204
3	188
4 ^a	---
4:30	224
5	206
5:30	210
6	215
7:30	192
8	194
9	197
10	185
11	185

^a Applied current of 0.89 amperes for 100.1 seconds

TABLE V
CALORIMETER CALIBRATION

Increase in Temperature, in microvolts, Caused by
the Application of Electrical Energy Equivalent to
Five Calories

Time, minutes	EMF, microvolts	Time, minutes	EMF, microvolts
0	81	0	157
1	51	1	157
2	77	3	172
3	100	4.5	195
4	57	5	182
5 [*]	---	6	176
5.5	154	7 ^{**}	---
6	190	7.5	220
6.5	238	8	239
7	226	8.5	288
8	249	9	355
8.5	223		
9	209		
10	220		
11	175		
12	220		
13	200		

* Applied current of 0.198 amperes for 100.3 seconds.

** Applied current of 0.198 amperes for 104.5 seconds.

TABLE V continued
CALORIMETER CALIBRATION

Increase in Temperature, in microvolts, Caused by the Application of Electrical Energy Equivalent to Five Calories			
Time, minutes	EMF, microvolts	Time, minutes	EMF, microvolts
10	340	17	508
11	330	18	532
12	317	19	500
13	334	20	548
14	335	21	555
15*	335	22	540
15.5	412	23	523
16	452	24**	512
16.5	508	24.5	600
		25	652
		25.5	695
		26	699
		27	690
		28	695
		29	672

* Applied current of 0.198 amperes for 100.0 seconds.

** Applied current of 0.198 amperes for 100.1 seconds

SAMPLE CALCULATION FOR ADSORPTION ISOTHERMS FROM %
TRANSMISSION VALUES

The amount of VMCH or VYHH adsorbed by one g of alumina is calculated from the following equation:

$$a = (A) (t/T) (1/10)$$

where a = the quantity of film former (milligrams) adsorbed by one gram of alumina

t = the difference in % transmission of the initial and the equilibrium concentration (mg per 20 cc of lacquer)

A = the difference in % transmission between the two control samples (mg per 20 cc of lacquer)

T = the difference in % transmission of the two control samples

An example is taken from Table XI, Part A and tabulated in Table V.

The calculations are:

$$a = (125) (98.2 - 95.5 / 100.0 - 94.5) (1/10)$$

$$a = 7.5 \quad 1.4 \text{ mg per g Al}_2\text{O}_3$$

The equilibrium concentration (c_{eq}) is the difference between the initial concentration (c_i) and the quantity of film former adsorbed by ten grams of Al_2O_3 (10 a) expressed in mg per 20 cc of lacquer.

$$c_{eq} = c_i - 10a$$

$$= 125 - 10(7.5)$$

$$= 50 \text{ mg per 20 cc of lacquer}$$

TABLE VI
INITIAL CONCENTRATION OF VMCH AND VYHH LACQUERS

Lacquer	Initial Concentration, per cent by weight	Density g per cc	Initial Concentration, ° mg per 20 cc of lacquer
VMCH	0.50	1.251	125
	1.00	1.252	250
	2.00	1.253	500
	3.00	1.253	750
	5.00	1.255	1250
VYHH	1.00	1.249	250
	2.00	1.248	500
	4.00	1.247	1000
	6.00	1.246	1500

°Converted from initial concentration in per cent
by weight using the following equation:

$$c_1 = (\%) (w) (v) (1000)$$

TABLE VII
INFRARED ANALYSIS OF THE ADSORPTION
OF VMCH BY ALUMINA

Per Cent Transmission Values for Selected Concentrations (Per Cent by Weight) of VMCH						
Part	Ethylene Dichloride Control	Sample Number			0.500% Control	
		1	2	3		
A	100.0	98.2	98.2	98.2	96.0	
					95.0	
B	0.500% Control	Sample Number			1.00%	
	1	2	3			
	96.0	94.5	95.2	95.6	91.5	
	95.0				91.5	
C	1.00% Control--	Sample Number			2%	
	1	2	3	Control		
	91.5	90.0	89.9	90.0	84.8	
	91.5				84.1	
D	2% Control	Sample Number			2%	
	1	2	3	Control		
	84.8	83.9	84.5	84.8	77.9	
	84.1					
E	3% Control	4% Control	Sample Number			3% Control
	1	2	3			
	105.6	100.0	101.0	102.1	102.1	94.1
						94.2

TABLE VIII
INFRARED ANALYSIS OF THE ADSORPTION
OF VYHH BY ALUMINA

Per Cent Transmittance Values for Selected Concentrations (Per Cent by Weight) of VYHH						
Part	Ethylene Dichloride Control	Sample Number			1.00%	
		1	2	3	Control	
A	109.5	100.0	100.6	99.4	95.0	
	107.5				97.4	
B	1.00%	Sample Number			2.00%	
	Control	1	2	3	Control	
	95.0	89.0	89.0	92.0	89.6	
	97.4				89.0	
C	3.00%	Sample Number			4%	
	Control	1	2	3	Control	
	82.3	75.0	69.0	73.7	74.1	
					71.1	
D	4% Control	5% Control	Sample Number			6% Control
			1	2	3	
	100.0	92.8	88.0	88.0	88.2	86.0
						87.0

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